

Carderock Division Naval Surface Warfare Center

Bethesda, Md. 20084-5000

CARDIVNSWC-TR-61-95/34 December 1995

Survivability, Structures, and Materials Directorate
Technical Report

2nd Workshop on Quantitative Methods for Evaluation of Paint Coating Performance, 1-3 November 1995, Summary Report

by
John Murray
Naval Surface Warfare Center

and
Michael P. Jurinski
CASDE Corporation

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Technical Report

**2nd Workshop on Quantitative Methods for
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by

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Naval Surface Warfare Division, Carderock Division

Annapolis MD 21402

and

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Alexandria VA

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INTRODUCTION

The 1st Workshop on Quantitative Methods for Evaluation of Paint Coating Performance, was held at the NSW Carderock Division, Annapolis Detachment on 27–28 October 1993. The objectives for the workshop were to (1) review the state-of-the-art especially in the area of electrochemical techniques, (2) provide a forum for sharing current technical progress by researchers in the field, (3) discuss alternative data analysis approaches and the difficulties in taking field measurements and (4) develop consensus on coating conditioning/accelerated testing techniques. The approximately 40 (non-NSWCCD) attendees listened to 26 presentations by internationally and nationally recognized experts from Academia, Research Centers and Industry during the two day session. Attendees were supplied with talk abstracts, copies of viewgraph materials and an attendance list.

Responders to the workshop follow-up survey presented several suggestions including an apparent need for follow-up workshops on a 2 year frequency. Therefore, this 2nd Workshop was held. The 1st workshop had been inadvertently scheduled the same week as the National Paint and Coatings Convention, therefore nearly eliminating attendance and participation by that technical sector. A review of the schedules of the various technical societies was made, the 1–3 November 1995 dates then selected as not directly interfering and a deliberate attempt was made to include commercial coatings personnel. Several other suggestions which were incorporated include increasing the talk lengths to 25 minutes with an additional 5 minutes for questions/discussion—and issuing a workshop summary report. Although the sessions were indeed long, the audience attention was maintained, as can be seen in Figure 1.

The approach selected for this summary report was to prepare a three- to four-sentence summary of each overview and talk while recognizing the severe limitations of this radical approach to abstracting. These summaries are presented in the order given as the DISCUSSION Section. Additionally, the author supplied presentation abstracts are included as Appendix A. Hard copy versions of the viewgraph and slide materials are not being supplied within this report. Most authors have expressed a willingness to supply a hard copy to those who request one. An attendance and address list is provided as Appendix B.

DISCUSSION

The workshop schedule is presented as Figure 2.

SUMMARY OF TALKS

OVERVIEW OF NAVY PAINT COATINGS

Mr. Albert Holder, NSWCCD

Mr. Holder's presentation provided an overview of the current status of the Navy's coating program and future needs. Paint coatings are the most cost effective means of protecting metals from corrosion in marine environments. The ideal coating for use in marine environments will be tightly adherent, have no pinholes, and provide a service life

of seven to ten years. Currently, powder coatings, high solids (low VOC) coatings, and waterborne coatings show promise of providing adequate protection while meeting the changing and increasingly stringent environmental restrictions that are being implemented.

SESSION 1—ELECTROCHEMICAL DC TECHNIQUES

OVERVIEW

Dr. Richard Granata, Lehigh University

Dr. Granata provided the overview of DC electrochemical techniques for evaluating coating performance and discussed potential problems associated with accurate measurements. DC techniques for evaluating coating performance include general area coating potential measurements, chronoamperometry, cathodic polarization defect testing, scanning reference electrodes, and electrochemical noise. A big problem with evaluating coating quality occurs as a result of the high electronic resistance of a good coating. Additionally, one needs to be aware that coating properties can vary, as a result of local inhomogeneities, coating thickness, or quality of coating cure, when evaluating the performance electrochemically. Extremely sensitive equipment is required for accurate measurements and is relatively inexpensive for dc measurements. Although ac techniques have appeared to be more attractive during the last 10 years, a steady interest remains in the use of the simpler dc techniques.

DC RESISTANCE TESTING OF FOOD CAN COATINGS

Mr. George Dittmeier, U.S. Army, Natick RD&E Center

Mr. Dittmeier presented preliminary results of efforts to correlate DC resistance testing of Army food can coating quality with EIS results previously performed on the same types of coatings. DC resistance tests provide a relatively inexpensive alternative to the EIS technique. Testing was performed on four coating systems; three candidates and one system currently being utilized. Results indicated that the DC resistance technique was able to differentiate between the four coating systems, but that the ranking was not quite the same as that provided by EIS. It was concluded that the DC resistance technique shows potential to be an inexpensive screening technique, but further development is still needed.

AN OVERALL METHOD FOR THE CHARACTERIZATION OF A COATING/METAL SYSTEM

Mr. Robert Cunningham, Valspar

Mr. Cunningham described the coating evaluation program being utilized at Valspar. This program includes DC polarization techniques to evaluate the substrate material for corrosion rates and metallic species concentration information, and EIS to evaluate the coating. Results of the DC and EIS tests are being collected into a database for future comparative evaluations of coating quality. It is anticipated that this will provide a quick and inexpensive method of evaluating coating quality.

LIFE PREDICTION OF AUTOMOTIVE COATINGS

Dr. Martin Kendig, Rockwell International

The automotive industry has a need for a rapid quantitative test to replace long term and accelerated exposure testing for paints. Results from proposed methods should be correlated with ASTM B117 (salt fog) test results, be able to confirm, for example, optimum methods for painting and should be able to at least qualitatively rank paints. Dr. Kendig described a newly proposed approach combining EIS, (used to evaluate percent water uptake and corrosion resistance of the coating) with a 24 hour cathodic disbonding test (used to evaluate the coating adherence to the substrate material). The method is being prepared as a draft for ASTM review.

EVALUATION OF NAVAL COATINGS BY ELECTROCHEMICAL NOISE METHODS

Professor Gordon Bierwagen, North Dakota State University

Professor Bierwagen presented the results from a 3 year, Navy funded effort to utilize electrochemical noise techniques to evaluate organic coatings on mild steel substrates. Electrochemical noise resistance values were used to rank coating performance and results were compared to the results of EIS, DC resistance, and cyclic salt fog testing. Numerical values for noise resistance showed good agreement to low frequency EIS modulus values as well as DC resistance values, and provided a relatively rapid ranking of coating performance. Future efforts will evaluate the effect of immersion electrolyte and thermal effects on coating performance.

EVALUATION OF COATING PERFORMANCE BY ELECTROCHEMICAL-IMPEDANCE SPECTROSCOPY (EIS) AND ELECTROCHEMICAL NOISE ANALYSIS (ENA)

Professor Florian Mansfeld, University of Southern California

Professor Mansfeld presented results of EIS testing of polymer coated metals which revealed such properties as water uptake, coating resistivity, degree of coating delamination, and corrosion rate at the metal/coating interface. Methods to evaluate electrochemical noise data, including noise resistance monitoring and frequency dependent spectral analysis were described. Accurate analysis of data requires the use of two identical electrodes to ensure similar electrode kinetics. Problems arising from dissimilar electrode kinetics were discussed. Professor Mansfeld cautioned that the information concerning coating performance by ENA is more limited than that available by EIS.

SESSION II—ELECTROCHEMICAL AC TECHNIQUES

OVERVIEW

Professor Ray Taylor, University of Virginia

Professor Taylor discussed the use of AC electrochemical techniques, including EIS, dielectric spectroscopy, harmonic analysis, cyclic voltammetry, and electrochemical noise in the determination of coating quality and performance. Key issues need to be ad-

ressed, such as how one predicts lifetimes and coating performance based on data analysis. Additional topics that need further discussion include determination of appropriate metrics (e.g., pore resistance, coating capacities, breakpoint frequencies, and phase angle data) and what are the limits of these metrics. Finally, it was stressed that while EIS can provide nearly all of the electrical and electrochemical information that can be acquired by purely electrical means, aesthetic functions of a coating system are also quite important and are dependent on more than just electrical and electrochemical events.

MEASUREMENTS OF ADHESION LOSS, DELAMINATION, AND INTERFACIAL WATER OF COATED METALS

Dr. Tinh Nguyen, NIST

Dr. Nguyen discussed a technique to measure adhesion loss and delamination due to absorbed water and a nondestructive, in situ method to determine the amount of water at the coating/metal interface. FTIR is a non-destructive technique in which an IR beam is sent through a germanium crystal, producing a unique spectra when reflected by a coating. The reflected spectra changes as a function of exposure time due to the increased absorbance of the IR beam as the coating degrades from water uptake. A new technique to measure the load required to pull the coating from the substrate was also described. This technique yields a plot of load vs. distance from scribe mark as a function of exposure time. These two techniques can be utilized to determine the relationship between adhesion loss and thickness of water at the interface.

STATUS OF NSWCCD ELECTROCHEMISTRY OF COATINGS TECHNOLOGY

Dr. John Murray, NSWCCD

The Navy needs to replace current subjective methods of evaluating coatings with automatic objective NDE methods. NSWCCD has been involved in the development of an improved portable, field compatible EIS system which can measure impedances to $10^{12}\Omega$ (See presentation summary by Dr. Greg Martinchek, Gamry Instruments, below). NSWCCD is also working to correlate long term exposure results to laboratory data and develop a database of the results. These efforts will help facilitate the use of NDE techniques in accurate coating performance evaluations.

EVALUATION OF POLYANILINE COATINGS BY IMPEDANCE MEASUREMENTS

Dr. Peter Spellane, AKZO Nobel Central Research

Polyaniline is an electroactive polymer which, in certain environments, has shown an ability to provide corrosion protection to steels and stainless steels. Polyaniline is most commonly made via persulfate oxidation of aniline. EIS data for polyaniline coatings show complex resistive-capacitive behavior, a low modulus of impedance, and a phase angle of -20° decreasing sharply at frequencies greater than 10^4 Hz. Degradation of the modulus and phase angle is seen after 24 hours exposure. It is clear that polyaniline does not act as a barrier coating. Further efforts will be focused on determining how the coating functions.

VARIABLE-AMPLITUDE GALVANOSTATICALLY MODULATED IMPEDANCE SPECTROSCOPY AS A NON-INVASIVE TOOL FOR ASSESSING REACTIVITY AT THE CORROSION POTENTIAL

Professor Mark Orazem, University of Florida

Professor Orazem described a galvanostatic EIS technique (as opposed to the more common potentiostatic technique) for assessing the reactivity of a surface that is non-invasive, does not perturb transient responses, and is sensitive to ongoing reactions. A technique such as this is ideal for evaluating processes such as transdermal delivery of drugs by iontophoresis, which is controlled by the amount of current through the skin and therefore could be changed by potentiostatically controlled measurements. An algorithm was developed and used to estimate the value of the impedance at the target frequency based on measurement at previous frequencies. By adjusting the amplitude of current perturbation at each frequency a desirable variation in potential can be achieved. This method also allows a reduced measurement time while yielding the same error structures as would be expected from potentiostatic measurements. Sensible EIS parameter values were presented from samples during the initial 2 days of solution exposure when the system under study was far from being stable.

THE EIS900 SYSTEM USED FOR COATINGS EVALUATION

Dr. Greg Martinchek, Gamry Instruments, Inc.

With SBIR Phase I funding, Gamry Instruments has developed a low cost, field portable EIS system that can be used to evaluate coatings on large structures. Older EIS systems have upper impedance limits on the order of $10^{10}\Omega$, were unable to make measurements on earth grounded structures, were not portable, and are considered to be very expensive. Gamry's new EIS900 system has achieved measurements of impedances of $10^{12}\Omega$ which is adequate for measuring coatings. The unit has an independent power source which allows the potentiostat to be floated, and the reduced system size, coupled with a laptop computer, allows the system to be transported to the field. This field-test system performs DC to 100 kHz measurements and has a price of \$9,000.00.

EXPERIMENTAL AND INSTRUMENTAL CONSIDERATIONS IN MEASUREMENTS OF EXTREMELY GOOD (HIGH IMPEDANCE) COATINGS

Dr. Robert Rodgers, EG&G Instruments, Princeton Applied Research (PAR)

Dr. Rodgers discussed the challenges involved in evaluating a good coating system due to its electrical properties and the operational limitations of the measuring equipment. An "ideal" potentiostat would have an infinite input impedance, no stray capacitance, draw no current from the cell, and have an infinite bandwidth. Unfortunately, real potentiostats have measurement limitations. It is possible to determine the limits by running an "air" experiment, with the high frequency data giving the capacitance limits and the low frequency data giving the resistance limits. When working with a good coating system, it is important to remember that the electrical properties may approach the measurement capabilities of the instruments. Dr. Rogers presented data from high impedance coatings obtained using the new PAR 283/1025 laboratory-based EIS system.

ANALYSIS OF POLARIZATION DECAY: THE FIELD PERFORMANCE OF COATINGS IN CAPE COD, MASSACHUSETTS

Dr. Ashok Kumar, U.S. Army CERL

Electrochemical techniques have been successfully used to determine corrosion rates, but not the condition of corrosion. The condition of corrosion is important to know for structures that are submerged, buried or otherwise not easily inspected. Dr. Kumar presented data from experiments in which coated samples were polarized for ten minutes, the current then interrupted and the changing voltage was recorded with respect to time. A good coating system showed high voltage decay rates, while bad/damaged coating systems had low decay rates. Also, as the amount of bare area increased, the decay rates decreased. The rate of polarization decay can thus be used to estimate the bare surface area. Data from structures in the field were also presented.

SESSION III—OTHER ASSESSMENT TECHNIQUES

OVERVIEW

Dr. Martin Kendig, Rockwell International

Dr. Kendig briefly discussed many of the non-electrochemical techniques that can be used to evaluate coatings. Radiative techniques include spectroscopy, microscopy, nuclear, scattering, thermography, and image analysis. Mechanical techniques that can be used include acoustics, surface energy analysis, microhardness, and adhesion testing. Additionally, non-Faradaic electrical techniques such as dielectrometry or Kelvin probes may be useful. Use of these techniques, however, raises issues of sensitivity, relevance, and data interpretation. Electrochemical techniques may be best for analyzing coating defects and water transport. A thorough analysis should use electrochemical methods to stimulate the system, with non-electrochemical methods used to monitor the results.

IMPROVED QUANTITATIVE FAILURE ANALYSIS FOR THE PREDICTION OF COATING SERVICE LIFE

Mr. J. Peter Ault, Ocean City Research

Current coating inspection techniques, such as ASTM D610, are visual, subjective by nature, and not useful for accurate lifetime predictions. Mr. Ault described an improved visual method being utilized by Ocean City Research to measure quantitatively, coating degradation and to make lifetime predictions based upon the results. Corroded areas are determined by laying a transparency over the sample and carefully coloring all of the corroded area. Image analysis techniques are then used to determine the percent area corroded quantitatively. Data are gathered at six months intervals for three years and are plotted as percent failure versus time. This method can then determine a coating lifetime based upon maximum allowable corroded areas.

QUANTITATIVE ANALYSIS OF SURFACE DEFECTS IN NATIONAL DEGRADATION USING IMAGE PROCESSING

Mr. Frederick Lee, R&D, South Florida Test Service

Mr. Lee discussed the use of digital image processing to analyze defects quantitatively. Digital image analysis techniques can increase the visibility of one portion or aspect of a sample. It can be used to identify feature sizes, develop stereographic views of the sample, and can provide quantitative analysis of colors, areas, etc. Digital image analysis techniques are able to provide vital information that visual observations might not be able to identify, thus providing greater certainty to failure analysis investigations.

AN IRON K-EDGE XANES STUDY OF IRON AND IRON OXIDES FOR THE CATHODIC DISBONDING OF FUSION BONDED EPOXY IN ALKALINE AQUEOUS SOLUTION

Dr. Inho Song, Case Western Reserve University

Dr. Song discussed the use of X-ray Absorption Near-Edge Structure (XANES) to analyze the cathodic disbondment of a fusion bonded epoxy from underground steel pipelines. Spectroscopic techniques can provide vital failure analysis information about a material system. X-ray absorption spectroscopy can provide information on elemental composition (from the position of the peaks), transition probability (from the intensity of the peaks), chemistry or oxidation states (from the change in peak position or intensity), and structure (from the change in absorption edge profile). This type of information was used to support oxide reduction and/or oxide dissolution as the mechanism of cathodic disbondment for the fusion bonded epoxy.

SENSING WATER SORPTION AND DIFFUSION IN MULTI-LAYER PROTECTIVE COATINGS VIA FLUORESCENCE PROBE TECHNIQUES

Professor John Torkelson, Northwestern University

Professor Torkelson discussed the use of fluorescence probe techniques to determine the amount of water absorbed by a polymer coating. This technique utilizes molecular "rotors" within the coating which either rotate around a bond or fluoresce when they absorb light of a particular wavelength. As these coatings absorb water, increased plasticization occurs, which results in an increase in bond rotation and decrease in fluorescence of the rotors. The particular rotors that Professor Torkelson employs show a direct proportionality between water absorbed and reduction of fluorescence. This proportionality allows quantitative determinations to be made even for multi-layer coatings.

METHODOLOGY FOR ASSESSING PERFORMANCE OF INHIBITIVE ORGANIC COATINGS

Dr. Richard Granata, Lehigh University

Dr. Granata presented the results of work assessing the performance of two types of epoxy coatings on an aluminum substrate in the presence of each of ten different inhibitors. EIS was used to evaluate the coatings. Tests were run with inhibitors added into the coatings and with inhibitors added to the test electrolyte using panels with and without intentionally introduced defects. In general, the inhibitors added to the electrolyte per-

formed better than those added to the coatings even when the inhibitor within the coating was at quite high levels. This is considered due to the easier transport mechanisms to the damaged area for the inhibitors added to the electrolyte.

ARE WE READY FOR PRIME TIME . . . A SKEPTICAL VIEW ON QUANTITATIVE TECHNIQUES FOR COATING EVALUATION

Dr. Simon Boocock, Steel Structures Painting Council

It is generally agreed that there is a great need to improve upon exposure and salt fog testing methods, NDE techniques such as visual inspections and dry film thickness measurements. While there is no one test that is good for all coatings, of the quantitative techniques available today, EIS has the highest level of use. However, EIS is limited by the level of experience required to perform and interpret data, acceptance of the technique by the coatings community, and high cost of equipment. Dr. Boocock believes that greater emphasis on the development and use of quantitative visual analysis methods is needed, coupled with statistical considerations in the experimental design phase. Better communication is still needed to transition techniques from laboratory to field usage.

SESSION IV—DATA ANALYSIS

OVERVIEW

Dr. W. Steven Tate, S.C. Johnson & Son, Inc.

Dr. Tate discussed some of the practical considerations to apply to data analysis when using EIS. It is important to remember that an electrochemical system is never a "constant." Variability is a big concern for making a proper assessment. Variations in scans from runs on "identical" samples demonstrate the need to apply statistical analysis methods to assess the error associated with EIS scans accurately. Additionally, a statistically sound number of replicate samples is needed for each variable to be tested. Finally, models used to analyze data should also be appropriately validated.

FEASIBILITY OF USING ARTIFICIAL NEURAL NETWORKS WITH EIS DATA ON COATED STEEL

Dr. Harvey Hack, NSWCCD

NSWCCD is developing an artificial neural network system to interpret data from EIS measurements on coatings. The goal is to develop a system that can give a good or bad decision on coating quality such that an inspector can make decisions without the extensive training and experience currently required to evaluate EIS data. The initial system has been able to successfully predict good vs. poor coatings. The neural network has also been able to determine whether measurement problems produced bad data. Future efforts may attempt to integrate the neural network with a measurement system.

MODERATED DISCUSSION – FRIDAY, 3 NOVEMBER 1995

The discussion session was aimed at addressing three issues: 1) Determination of initial coating quality, including techniques to assess substrate surfaces prior to a coating application and techniques that can be utilized after the initial coating, 2) Screening methods – how does one rank/test new coatings, and 3) How does one assess the performance of new coatings on site.

Prior to application of a coating, the primary method of assessing the quality of surface preparation remains visual observation. It was generally agreed that a portable instrument that characterizes the surface preparation, including surface roughness and surface contamination, is needed. Dry film thickness and wet film thickness measurements remain the most widely used methods of determining coating quality. New techniques need to be implemented. The applicability of using fluorescence techniques to make on-line determinations of the cure quality of epoxies was discussed.

The second issue dealt with test techniques that could be used to evaluate new coatings and rank performance. Currently, ASTM B 117 (Salt Fog Testing) remains the primary method of screening/ranking coatings. Proposed alternatives to ASTM B 117 included cathodic disbondment, spark tests, EIS, peel tests, near IR, and EC noise. A major discussion topic with this issue is "what constitutes failure?". It was generally agreed that failure criteria had to be defined by the individual user on a case-by-case basis.

The third issue dealt with assessing new coatings on site. Techniques need to be sensitive enough to detect events such as the onset of blistering. New inspection equipment should be packaged similar to the Gamry field EIS unit. Another topic of discussion within this issue dealt with inspection criteria. Does one need to inspect all coated areas or can statistical methods be applied to reduce inspection requirements?

Another issue was raised by a coating manufacturer, who asked what the manufacturers need to do to prove that new products being developed are superior to current products. While several suggestions were offered and discussed, no real conclusive test protocol was provided.



Figure 1a. Dr. Tinh Nguyen; NIST on Coating Adhesion.



Figure 1. At the Workshop in the Melville Room.

2nd WORKSHOP ON QUANTITATIVE METHODS
FOR PREDICTING COATING PERFORMANCE

PROGRAM OUTLINE

1 November 1995

08:00 - 09:00 Registration
09:00 - 09:05 WELCOME,
 Mr. Ivan Caplan (NSWCCD)
09:05 - 09:10 General Comments,
 Dr. John Murray (NSWCCD)
09:10 - 09:40 OVERVIEW of Navy Paint Coatings,
 Mr. Albert Holder (NSWCCD)

SESSION I - ELECTROCHEMICAL DC TECHNIQUES

09:40 - 10:20 OVERVIEW,
 Prof. Richard Granata, Director, Corrosion Laboratory,
 Zettlemoyer Center for Surface Science Studies, Lehigh University

SHORT R&D PRESENTATIONS - RECENT DATA

10:20 - 10:50 "DC Resistance Testing of Food Can Coatings"
 Mr. George Dittmeier, US Army Natick RDE Center
10:50 - 11:20 "An Overall Method for the Characterization of a Coating/Metal
 System",
 Mr. Robert Cunningham, Valspar
11:20 - 11:50 "Life Prediction of Automotive Coatings"
 Dr. Martin Kendig, Rockwell International
11:50 - 13:00 LUNCH
13:00 - 13:30 "Recent Studies of Marine Coatings by Electrochemical Noise
 Methods",
 Prof. Gordon Bierwagen, North Dakota State U.
13:30 - 14:00 "Evaluation of Coating Performance by EIS and ENA",
 Prof. Florian Mansfeld, USC

SESSION II - ELECTROCHEMICAL AC TECHNIQUES

14:00 - 14:40 OVERVIEW,
 Prof. Ray Taylor, U. Virginia
14:40 - 14:55 BREAK

Figure 2. Program Outline.

SHORT R&D PRESENTATIONS - RECENT DATA

- 14:55 - 15:25 "Measurements of Adhesion Loss, Delamination and Interfacial Water of Coated Metals"
Dr. Tinh Nguyen, NIST
- 15:25 - 15:55 "Status of NSWCCD Electrochemistry of Coatings Technology",
Dr. John Murray, NSWCCD
- 15:55 - 16:25 "Evaluation of Polyaniline Coatings by Impedance Measurements",
Dr. Peter Spellane, Akzo Nobel Central Research
- 16:25 - 17:30 GROUP MODERATED DISCUSSION; ASTM-G-1.11

2 November 1995

- 08:30 - 09:00 "Variable-Amplitude Galvanostatically Modulated Impedance Spectroscopy as a Non-Evasive Tool for Assessing Reactivity at the Corrosion Potential",
Prof. Mark Orazem, U. Florida
- 09:00 - 09:30 "The EIS900 System Used for Coatings Evaluation",
Dr. Greg Martinchek, Gamry Instruments, Inc.
- 09:30 - 10:00 "Experimental and Instrumental Considerations in Measurements of Extremely Good (High Impedance) Coatings"
Dr. Robert Rogers, Princeton Applied Research Corp.
- 10:00 - 10:30 "Analysis of Polarization Decay"
Dr. Ashok Kumar, US Army CERL
- 10:30 - 10:45 BREAK

SESSION III - OTHER ASSESSMENT TECHNIQUES

- 10:45 - 11:25 OVERVIEW,
Dr. Martin Kendig, Rockwell International

SHORT R&D PRESENTATIONS - RECENT DATA

- 11:25 - 11:55 "Improved Quantitative Failure Analysis for the Prediction of Coating Service Life",
Mr. J. Peter Ault, Ocean City Research
- 11:55 - 13:00 LUNCH
- 13:00 - 13:35 "Quantitative Analysis of Surface Defects in Natural Degradation Using Image Processing"
Mr. Frederick Lee, R&D South Florida Test Service

Figure 2. Program Outline (continued)

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- | | |
|---------------|--|
| 13:35 - 14:05 | "Specification of Navy Coatings for Topside and Underwater Hull Applications",
Mr. Keith Lucas, NRL |
| 14:05 - 14:35 | "XANES Study of the Iron Interface Beneath Fusion Bonded Epoxy",
Dr. Inho Song, Case Western Reserve |
| 14:35 - 14:55 | BREAK |
| 14:55 - 15:25 | "The Use of Fluorescence Spectroscopy in Coating Degradation",
Prof. John Torkelson, Northwestern U. |
| 15:25 - 15:55 | "Methodology for Assessing Performance of Corrosion Inhibitive Organic Coatings",
Prof. Richard Granata, Lehigh U. |
| 15:55 - 16:25 | "Are We Ready for Prime Time - A Skeptical View on Quantitative Techniques for Coating Evaluation",
Dr. Simon Boocock, Steel Structures Painting Council (SSPC) |

SESSION IV - DATA ANALYSIS

- | | |
|---------------|---|
| 16:25 - 17:05 | OVERVIEW,
Dr. W. Steven Tait, S.C. Johnson & Son, Inc. |
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SHORT R&D PRESENTATIONS - RECENT DATA

- | | |
|---------------|---|
| 17:05 - 17:35 | "Feasibility of Using Artificial Neural Networks with E.I.S. Data From Coated Steel",
Dr. Harvey Hack, NSWCCD, Code 613. |
| 17:35 - 18:00 | GROUP MODERATED DISCUSSION |

3 NOVEMBER 1995

- | | |
|---------------|---|
| 08:30 - 11:30 | MODERATED DISCUSSION,
Dr. Harvey Hack, Discussion Leader |
|---------------|---|

"And the questions are... do any of these measurements mean anything regarding the paint condition, the paint life, the paint life predictions?"

- | | |
|-------|---|
| 11:30 | Adjourn until Workshop III (Oct. 1997 at Carderock, MD) |
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Figure 2. Program Outline (continued).

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APPENDIX A
AUTHOR SUPPLIED TALK ABSTRACTS.

MARINE COATINGS

Albert Holder, Jean Montemarano

Naval Surface Warfare center, Carderock Division
3A Leggett Circle
Annapolis, MD 21402-5067

ABSTRACT

Advances in coating technology today are driven by environmental regulations. The coating industry faces a challenge in complying with a variety of governmental rules while trying to provide the customer with high performance products. How to meet ever increasing stringent environmental demands while producing a coating with equal or improved performance properties is the concern. A recent article in the Chemical Week estimates that three-fourths of the research and development effort in the coating industry is focused on developing coatings that are "environmentally friendly," - comply with present or future environmental regulations. These resources would normally have been directed to improving coating product performance through advancements in coating technology.

OVERVIEW

ELECTROCHEMICAL DC TECHNIQUES

Richard D. Granata

Zettlemoyer Center for Surface Studies
Lehigh University
Bethlehem, PA 18015

ABSTRACT

Evaluation of protective organic coatings by electrochemical DC techniques were reviewed.

The problems associated with the measurement of low level signals in electrochemical systems were described using examples of an uncoated interface, H^+ -ion reduction on Pb, and the glass electrode for pH measurements—Small exchange currents for electrode reactions and resistive, non-faradaic barriers. Appropriately designed, high impedance equipment and cell design must be used when measuring low level electrochemical systems.

To provide background for the subsequent presentations, a generic description of a metallic substrate/organic coating system was provided including galvanized/phosphated and bare steel substrates. Emphasis was placed on blast-cleaned, bare steel substrates. Degradation loci were identified at the metal, oxide and coating interfaces. Coating degradation factors were reviewed including physical damage, exposure to ultraviolet light, liquid water, humidity, salts, atmospheric sulfur/nitrogen oxides and temperature, and transient/cyclic phenomena. Mechanisms of coating deterioration were discussed.

Laboratory studies were described. Resistance measurements have shown inhomogeneity of polymer coatings suggesting possible differences relating to cure of various coatings types. Description was made of D-type and I-type coating areas corresponding to their direct or indirect response to osmotic effects. Mapping potentials on a coated surface suggests difference in electrochemical nature of substrate areas or may be related to the coating resistivity.

Additional techniques described included; chronoamperometry—a current versus time response to small applied potential; and cathodic polarization defect testing—a measure of uncoated, active metal area. The caveat of damage due to applied potential or current was described. The techniques of Kelvin probe surface measurements and electrochemical noise were introduced for subsequent presentations/discussions.

ACKNOWLEDGEMENT: The author is grateful for the long-term support of organic protective coatings research by the Office of Naval Research.

Mr. George Dittmeier
US Army Natick RD&E Center

Abstract

Tin Coating Testing By Means of DC Resistance

Initially Electrochemical Impedance Spectroscopy (EIS) was used by the US Army to test three food can coating candidates. Because of budget and training time considerations, it was decided to substitute DC resistance testing for further can coating testing. The key DC test instruments required to successfully use this method were two Keithley Electrometers. The objective of the initial phase of his testing program was to: a. develop the technique, and b. correlate DC resistance results with EIS results previously obtained on the same coatings. Accompanying slides show that this correlation was successful. The next phase was to attempt to use the DC resistance technique as a quality control method to monitor food can coating quality in the plant. A substantial sample of production cans representing six months output were DC resistance tested. Of these, 20% rated subpar vs, baseline data obtained on prototype cans. However, due to the substantial corrosion protection provided by the heavy tin plate substrate, no important can corrosion (i.e., perforations) was reported from the field on filled cans after two years. We tentatively concluded that using the DC/AC resistance testing method to predict field failures needs further work to become an acceptable QC tool. This means establishing the test failure criteria that will predict field can failures.

MODELING OF ELECTROCHEMICAL POLARIZATION DECAY OF COATED STEEL

Ashok Kumar, Vicki Van Blaricum, and Jeffrey H. Boy
U.S. Army Construction Engineering Research Laboratories (USACERL)
P.O. Box 9005
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The U.S. Army Corps of Engineers owns and maintains a vast network of structures along the nation's waterways, including navigational locks, dams, piers, and bulkheads. These structures represent a huge capital investment and many of them have been in service for 30 or more years. The maintenance engineer needs to know the corrosion status and overall condition of such structures to make sound repair and replacement decisions. Visual inspection is usually conducted if the surface is exposed and accessible. Ultrasonic, pit depth, and eddy current measurements are conducted to determine the corrosion condition. However, when the structure is immersed in water or buried in soil, remote corrosion condition assessment and corrosion rate assessment techniques are needed.

Electrochemical measurement techniques, such as the polarization resistance and the determination of the Tafel plots, have traditionally been used to measure the corrosion rate. There are two main problems with these techniques. One of the problems is that the area of the polarized steel needs to be accurately estimated to determine the corrosion rate per unit area. For large continuous structures, such as buried pipelines, isolation of a local area of known dimensions is difficult. The second problem is that the polarization resistance measurements only tell us the present corrosion rate. They do not give any information about the corrosion condition. However, electrochemical polarization decay measurements in the time domain have the potential to overcome these drawbacks. The polarization decay rate is only influenced by the local area surrounding the reference electrode, and the results can be correlated to the condition of the surface.

Electrochemical techniques have been developed and refined by USACERL to nondestructively evaluate the corrosion status of coated steel structures that can not be visually inspected. This includes steel submerged in water, buried in soil, or encased in concrete. These techniques included: (1) measurement of electrochemical polarization decay (2) electrochemical impedance spectroscopy analysis and (3) measurement of a polarization resistance. These techniques were successfully modeled using laboratory results and utilized in the field to estimate coating conditions and to predict the long term performance of coatings systems.

USACERL utilizes two test sites for the long term evaluation of coated steel submerged in sea water. The Buzzard's Bay, Cape Cod, MA, test site was installed in October 1974 and consisted of three rows of 22 steel H pilings with various coating systems, both with and without cathodic protection. The La Costa Island, FL test site, installed in January 1971, contained steel H pilings, steel pipe pilings, and prestressed concrete pilings. Some of the pilings from both sites have been removed in order to perform more detailed evaluations. The mean yearly water surface temperature at the La Costa FL test site is 75°F (24°C). The mean temperature at the Buzzard Bay, Cape Cod MA test site is approximately 60°F (15°C).

Electrochemical polarization measurements were conducted to nondestructively determine the bare steel area in the immersed area of the coated piles at the Cape Cod, MA test site in 1995.

**AN ELECTROCHEMICAL METHOD FOR THE ANALYSIS OF ORGANIC
COATING-METAL SUBSTRATE SYSTEMS**

ABSTRACT

This paper describes a method designed for the characterization of an organic coating - metal substrate system utilizing both AC and DC electrochemical measurements in conjunction with other physical and instrumental methods. The purpose of this method is twofold, 1) provide a time saving screening tool to assist formulators during the coating development process, and 2) provide insight into adhesion, delamination and corrosion related problems. The method can be subdivided into three main subsections; 1) substrate analysis by DC polarization, 2) coating/substrate analysis by Electrochemical Impedance Spectroscopy, and 3) database correlation of results. The first two sections are performed concurrently with the current physical/instrumental methods employed by the industry for coating systems analysis while the third section is product-database specific. While method development is still proceeding, the initial stages have been completed and the results are encouraging. In the future it is hoped that the results obtained by use of this method will correlate with the industry standard pack tests, at least partially eliminating the need for such a time and labor intensive test. The projected savings in time, manpower and money are well worth the initial investment of equipment and time in comprehensive database building as the cycle time of product formulation and troubleshooting will be considerably reduced.

RAPID ELECTROCHEMICAL ASSESSMENT OF AUTOMOTIVE PAINT

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A need exists to rapidly predict the life of organic coatings and paints on steel. For a number of years electrochemical impedance methods have been proposed although a detailed protocol for their application in very short times for assessing automotive paint has not been forthcoming.

The development of a rapid electrochemical test for the corrosion resistance of painted steel requires consideration of the corrosion mechanism of painted steel. Painted steel corrosively degrades by (1) penetration of water and ions through the coating, (2) initiation of anodic dissolution at defects, as driven by (3) cathodic reduction of water at the metal surface adjacent to the coating defects. The cathodic reduction of water and oxygen at regions adjacent to coating defects produces sodium hydroxide which propagates the loss of adhesion of the organic film. Any rapid electrochemical test must take into account these three aspects of coating failure. Whereas the ability of electrochemical impedance to detect paint degradation at early times remains more or less uncontested, its ability to detect extensive disbonding remains doubtful. Hence, the test methodology developed at Rockwell entails two rapid tests. Electrochemical impedance for coated samples obtained at initial times and after 24 h exposure of the test specimen to 0.5 M NaCl provides a measurement of the water uptake and the rate of corrosion initiation at defects in the coating. A 24 h electrolytically accelerated cathodic disbonding test evaluates the propensity of the coating to disbond and thereby propagate the corrosive failure of the coating.

Over 100 steel coupons painted with a variety of paints with varying conditions of surface treatment were evaluated using two 24 h electrochemical tests. The results were compared to longer term (up to 1000 hour) salt fog exposure using ASTM B 117. Failure of the respective samples in the salt fog test were defined in terms of either a scribe pull back TTF(PB), a visual assessment, or a combination thereof, TTF. Stepwise regression revealed that the TTF(PB) and TTF could be correlated with the 24 h corrosion resistance, R_{cor} , the apparent disbond rate, dx/dt , and the 24 h water uptake. R_{cor} and water uptake were determined from the impedance analysis at 0 and 24 h and the apparent disbond rate was determined from a 24 h disbonding test.

Practical use of this method for routine characterization of the painting process requires rapid analysis of the impedance spectra for replicate samples (at least five replicates are usually considered) and replication of the cathodic disbond test. A computerized algorithm was developed for rapidly evaluating the key parameters (coating capacitance and R_{cor}), and a multipotentiostat system was used to replicate the disbonding test.

Salt fog testing has come under some criticism regarding its relevance to coating life. Nevertheless, it is recognized as a standard. Decreased salt fog life can identify when the painting process goes out of specification. The correlation of a short (24 h) test to a longer term salt fog exposure represents a first, but necessary, step in industrializing electrochemical test methods. The basic principles of this approach, which are

(1) short exposure of the test piece to the simulated environment followed by impedance analysis to detect early degradation and water uptake,

(2) evaluation of the cathodic disbonding rate in the relevant environment,

can clearly be applied to environments and conditions other than immersion in 0.5 M NaCl. For example, one cycle of a cyclic exposure test with or without conditions of uv irradiation or mechanical impact could just as well be substituted for the 24 hour immersion considered here.

Abstract for 2nd Workshop on
QUANTITATIVE METHODS FOR EVALUATION OF PAINT COATING PERFORMANCE
to be held at Naval Surface Warfare Center, Carderock Division, Annapolis Detachment, Annapolis, MD
Nov. 1-3, 1995

Evaluation of Naval Coatings by Electrochemical Noise Methods

Work performed at North Dakota State University, Fargo ND 58015

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This program began as a two year project funded through ONR by Dr. A. J. Sedriks to verify the usefulness of the Electrochemical Noise Methods (ENM) as developed for application to organic coatings at Sherwin-Williams by Dr. Brian Skerry and Dr. Dave Eden (later of CML, Manchester, UK). This was done in the examination of two sets of marine coatings, a 3-coat alkyd system and a 3-coat epoxy-polyamide system, both chosen with the help of Jean Montemerono of NSWC. The multiple sample set of coatings on shot blasted mild steel substrates were examined continuously in 3% NaCl more than 120 days by ENM, while simultaneously examining their performance by EIS, dc resistance, and ProhesionTM cyclic salt fog testing. ENM data on multiple samples as expressed by the noise resistance, R_n , gave the known ranking, epoxy > alkyd, that prior performance data had shown, as well as shown in ProhesionTM testing and hot salt water immersion. The numerical values for R_n showed good agreement to low frequency EIS modulus values and R_{dc} values. However, the R_n for the individual sample pairs showed variation due to sample-to-sample variations in sample preparation, especially film thickness variations from the standard electrostatic spray application used in sample preparation. In this part of the work a derivation was developed which put the R_n calculation on a firmer theoretical basis than the qualitative arguments originally put forth by Eden and co-workers.

We have also initiated an effort to compute low frequency noise impedance (Z_n) values from the ENM data by spectral analysis methods. We have acquired data to show that by both FFT and MEM methods, we can determine low frequency Z_n data which is comparable to EIS data acquired by an imposed signal. We are currently developing methods of interpreting this data *vis a vis* our R_n , EIS and R_{dc} results, as well as our other qualitative evaluations of marine coatings.

When we began our ENM work, no statistical examination of the reproducibility of the data from such measurements has been published. In the data we present, we have done such a systematic analysis of important experimental variables in such systems. We have examined the method for accuracy and reproducibility with respect to sample preparation, sample immersion, and metal substrate preparation. We have taken several marine coatings systems typical of Navy use, and prepared duplicate samples of coating-metal systems, and examined them under the same immersion exposure. The variables we are thus considering for reproducibility are paint application (in three coat systems) metal panel preparation (grit-blasted steel) and immersion conditions. We present ENM data with respect to immersion time on the values of noise voltage standard deviation σ_v , noise current standard deviation σ_i , and the noise resistance R_n as given by σ_v/σ_i . The variation among supposedly identical sample pairs in identical immersion monitored under identical conditions is presented. The statistics of the time records of the data are also considered, and the variations with respect to specific coatings classes are also considered within the limits of the data. Based on these data, comments with ENM on coated metal systems as a predictive test method are presented, and special considerations which must be made to properly utilize the method for coating ranking and lifetime prediction.

We have also considered various immersion electrolytes in our ENM and EIS studies for the emulation of various exposure conditions. Dilute Harrison's solution has become the standard electrolyte for emulating the type of atmospheric exposure seen by industrial maintenance and automotive coatings, and we are using this in our studies of Naval aircraft coatings (sponsored by an AASERT grant supplemental to our ONR grant through Dr. Sedriks' office). In these studies, we have been able with ENM to see the differences between electrodeposition and standard spray primers and also to differentiate between chromate and non-chromate pretreatments of aircraft alloys. Other studies for other sponsors has helped us further examine the effects of immersion electrolyte, but the interaction between the electrolyte and the coating/metal system still needs to be quantified and modeled in a more satisfactory manner.

Our research group has also begun to examine thermal effects on coating performance, and has discovered that thermal transition effects within the immersed coating have significant effects on the electrochemical behavior of coating/metal systems. Previous work by Mills and Mayne had identified a link between R_{ct} and immersion temperature, and seen distinct changes in R_{ct} vs. T data at temperatures about the film glass transition temperature, T_g , values. We have extended this to ENM and EIS results on film performance vs. temperature, using dynamic mechanical thermal analysis (DMTA) and dynamic scanning calorimetry (DSC) on identical films to quantify the thermo-mechanical changes in the film. The distinct effects of the T_g transition on film transport properties, the effects of film water uptake, and film composition effects have been observed. Water/electrolyte uptake plasticizes the film, and can significantly decrease the T_g of the immersed film versus the dry film, and we are currently comparing thermo-mechanical estimates of electrolyte uptake with estimates from electrochemical measurements. We plan to supplement these measurements with film weight changes upon immersion to further quantify water/ electrolyte intrusion effects on system performance. Current film studies utilizing the combined thermal and electrochemical analysis of the film/metal system has identified unique, irreversible changes in films that have specific polar or ionic composition effects (e.g. epoxy and ionomer polymer based coatings). We are trying to determine how to properly use the thermal effects to accelerate failure/lifetime testing of coatings, and to understand how film corrosion protective performance and its degradation in immersion are altered by thermal effects and electrolyte intrusion into the films.

As an extension of the sample variation effects we have observed in our initial multiple-sample set studies of marine coatings, we have begun studies of electrode asymmetry in ENM experiments. We are beginning to examine the effects of defects on a single panel in ENM measurements with multiple "nominally" identical panels in a single exposure. From N panels, we can form $N(N-1)/2$ independent pairs of panel by connecting them independently to our ENM measurement equipment. This will also allow us to achieve better statistics with minimal sample preparation. Work by a summer undergraduate student supported by another program began this past summer on this problem, and we are extending our studies in this area. In this study we are addressing the study of locally "failed" coatings, to determine the effects of defects upon our ENM data, and to possibly use ENM to identify local failure in coatings.

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Evaluation of Coating Performance by Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise Analysis (ENA)

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Abstract

Analysis of EIS data for polymer coated metals results in fit parameters from which information concerning coating properties such as water uptake and coating resistivity as well as degree of coating delamination and corrosion rates at the metal/coating interface can be determined [1]. Analysis of electrochemical noise data can be performed by statistical methods resulting in values of the noise resistance R_n or by evaluation of the frequency dependence in power spectral density plots or spectral noise plots introduced by Mansfeld and Xiao from which the spectral noise resistance R_{sn}^0 can be determined [2,3]. Information concerning coating performance obtained by ENA is more limited than that available from EIS.

It has been shown recently that simultaneous collection of potential and current noise data allows evaluation of the frequency response in more detail [2-4]. This approach makes necessary the use of two electrodes of the same material. If it is desired to collect EIS and ENA data for the same system at a remote test site, EIS data have to be collected for the same two-electrode system. The experimental approach used by the authors to collect EIS and ENA from seawater test sites at Port Hueneme, FL and Key West, FL by remote control from CEEL in Los Angeles, CA will be described and illustrated for 13 paint systems applied to steel [2].

Collection of electrochemical potential and current noise data for determination of R_n and evaluation of the frequency dependence of characteristic noise parameters requires the use of two identical electrodes, i.e. electrodes with the same electrode kinetics. When the requirement of the use of identical electrodes is not fulfilled, complications can arise in the interpretation of noise data [5]. Similar problems can occur in the measurement and interpretation of impedance spectra as will be demonstrated for polymer coated steel, where the properties of the electrode with the more protective coating dominate the experimental results. An equivalent circuit for asymmetric electrodes is being proposed which allows monitoring of coating degradation even if only one electrode

has developed significant coating damage [5]. Experimental data for three different coating systems on steel exposed to artificial and natural seawater for several months will be presented to illustrate this problem. A significant decrease of R_n was observed only when damage to the coating on both electrodes had occurred. Experiments with model electrodes will illustrate the problems arising in the analysis of EIS and ENA when coating damage has not developed in the same manner for both electrodes. In this case ENA cannot detect coating damage occurring for only one electrode [2,5]. However, data analysis is still possible for EIS data although only in a qualitative manner [5].

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An Overview of AC Electrochemical Techniques for the Characterization and Assessment of Organic Coatings

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There are numerous electrochemical techniques which might be classified as AC, however this talk will focus on the most common AC method applied to the investigation of organic coatings on metals, i.e. Electrochemical Impedance Spectroscopy (EIS). EIS has had many successes in the detection and characterization of breakdown phenomenon associated with organic coatings on metals exposed to aqueous environments. However, the author raises the question as to whether we may be expecting too much from a single technique. For example, there are many reported instances where blister formation has been observed visually, yet was not detected by conventional EIS measurements. Although this particular situation might be explained by low ionic conduction in the film, the larger questions become: to what extent should I rely on EIS for the characterization of a coated metal and what parameter or characteristic should I use to predict lifetime "performance"? This talk pointed out that in some instances, the difficulty in relating EIS data and coating performance may be rooted in the definition of "failure". If failure is defined as the development of permanent ionic pathways, then EIS could be well suited for the task, but if failure is defined as the expression of metal substrate ions into solution or loss of gloss, etc., then EIS may not be the panacea that some would like. The author concludes by reminding the audience of the many environmental variables, variables within the coating system (coating/substrate/surface treatment) and the many modes of coating failure and asks whether it is wise to expect any single characterization method to tell us what is happening to the system. The sensible approach to characterization and lifetime prediction is to develop a more comprehensive failure model (similar to that of Kendig) which might include, EIS data, cathodic disbondment data, wet state adhesion performance and add to it, defect data, and perhaps other information from yet other techniques. This model would be adjusted per coating system.

Measurements of Interfacial Water, Adhesion Loss and Delamination of Coated Substrates

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Abstract: This paper presents two methods for quantifying the degradation of organic-coated substrates during exposure. The first method, which is based on a two-layer model derived from the evanescent wave theory, measures in situ the amount and thickness of the water layer at the coating/substrate interface. The model takes into account water at the coating/substrate interface, water taken up by the coating within the probing depth of the evanescent wave, and change of the penetration depth as water displaces the coating from the substrate. This method can measure the interfacial water layer for either transparent or opaque coating of any thickness. The theoretical basis of this method has been described (1,2), and its use for studying interfacial water for a coating/iron system has been illustrated (3,4). The applications for measuring the diffusion of water through a coating film adhered to a substrate (5), the water layer at the organic film/hydroxylated interface (6,7), and the effects of surface treatment on polymer/SiO₂ interfacial water (8) have been presented.

The second method measures the rate of cathodic delamination and adhesion loss of coated metals exposed to water or corrosive environments. The apparatus consists of a base plate bolted to a computerized universal testing machine, a fixed slider (rail) attached to the base plate, and a moving slider that glides along the rail. Clamps on the moving glider hold the test specimens in place. This test is sensitive, quantitative, and reproducible; the coefficient of variation of measurements is less than 10 percent. The applications of this method for measuring the adhesion loss and cathodic delamination of powder epoxy coatings on steel exposed to alkaline electrolytes (9), determining the effect of surface treatment on adhesion loss of coatings (8), and studying failure mechanisms of coatings (9,10) have been demonstrated. Its use for measuring dry peel adhesion of primers and finish coat on steel has been also described (11). Information obtained by these two methods is valuable for studying the durability of coated materials.

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Status of NSWCCD
Electrochemistry of Coatings Technology

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The NSWCCD program on applying electrochemical (EC) techniques for evaluation of organic coatings has continued to pursue the challenges of the two primary tasks. The first task has involved overseeing the development of a field portable, electrochemical impedance spectroscopy (EIS) system with enhanced measuring capabilities. The apparent need for measurements in the $10^{12} \Omega$ range was based on conclusions from modeling efforts¹ which suggested the EIS low frequency break-point may be the proper parameter for determining and monitoring the initiation of the coating breakdown process. The resulting Gamry EIS900 system, developed partially with SBIR funding appears to satisfy many of the requirements and will be discussed to a very limited extent. The second task is the development and maintenance of an EC and EIS data base for the various organic coatings utilized in Navy applications. This effort has concentrated on coatings for immersion service. Data from several epoxy based systems have been published previously and three groups of samples have been continued on test through approximately 5 years. The data have been recently upgraded and will presented and discussed. The changes in thinking regarding the application of EC techniques will also be presented.

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Evaluation of Polyaniline Coatings by Impedance Measurements

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In 1981 Mengoli et al reported that a coating prepared by the anodic synthesis of polyaniline on iron provided protection to the metal and exhibited semiconductor properties (J. Appl. Polym. Sci. 1981, 26, 4247). The corrosion protection of stainless steel substrate by electrochemically prepared polyaniline was described by DeBerry (J. Electrochem. Soc. 1985, 132, 1022). In that work, polyaniline was electrodeposited on ferritic stainless steels, and the possibility of electron transfer between the electroactive polymer and the metal substrate was presented.

We have investigated the protection provided to cold rolled steel by solution cast films of polyaniline-emeraldine base, PANI-EB. Our interests are twofold: does PANI-EB protect steel from corrosion, is there evidence of electronic interaction between the substrate and the coating, and, ultimately, how are these phenomena related.

We measured the electrochemical impedances of PANI-EB coatings on CRS and compared them to the impedance behavior of clear epoxy and chromate-containing epoxy resin coatings. In these electrochemical cells, the coated steel is the working electrode, a graphite rod is the counter electrode, SCE is the reference electrode, and 5% NaCl forms electrolyte solution. We used Gamry CMS 100 and CMS 300 corrosion system software running on a Compaq 486/33 computer for these measurements.

EIS data for the clear epoxy resin coating indicate a purely capacitive coating which deteriorates over 24 hours. The EIS data of the PANI-EB coating indicate a more complex resistive-capacitive behavior: the modulus of impedance is low, decreasing from 160 to 20 ohms, and the phase angle is approximately -20° , decreasing sharply at frequency greater than 10^4 Hz. After 24 hours, some degradation of the modulus and phase angle is seen.

The PANI-EB coating appears to be fundamentally unlike the epoxy coating: EIS data of the former give no indication of barrier properties, while data of the latter suggest a good barrier.

Variable-Amplitude Galvanostatically Modulated Impedance Spectroscopy as a Non-Invasive Tool for Assessing Reactivity at the Corrosion Potential

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Abstract

An algorithm is described in which galvanostatic regulation of electrochemical impedance measurements is conducted with an amplitude of current perturbation that is adjusted at each frequency to yield a desired variation in potential. Measurements at previous frequencies are used to estimate the value of the impedance at the target frequency. The algorithm was implemented using LabView for Windows® on an IBM-compatible computer. Experimental results illustrate artifacts which can arise as a result of galvanostatic measurement with a fixed current amplitude or as a result of potentiostatic measurements for systems with a changing corrosion potential.

Experimental results using the new algorithm will be presented for a copper electrode subjected to a high-velocity impinging jet of synthetic sea-water. The corrosion potential was monitored continuously, and impedance measurements and optical video microscopy images were obtained at specified intervals. Measurement models were used to assess the stochastic and bias error structure of the impedance measurements. The copper/synthetic sea-water system chosen to illustrate the benefits of the variable amplitude potentiostatic algorithm was strongly affected by the formation of salt and oxide films. The corrosion potential of a freshly polished copper electrode submerged in electrolyte changed rapidly at first due to the formation of films, then reached a pseudo steady-state condition after a period of several days. In spite of the rapid change in surface reactivity, bias-error-free impedance measurements could be obtained even within the first hours of immersion. Variable-amplitude galvanostatically modulated impedance spectroscopy is shown to be a suitable non-invasive tool for assessing the reactivity of the electrode during a long-term measurement of the corrosion potential.

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Dr. Greg Martinchek, Gamry Instruments

Abstract

The EIS900 EIS System used for Coatings Evaluation

EIS (Electrochemical Impedance Spectroscopy) has become a preferred technique for the evaluation of coatings on metals. Unfortunately, measurements on coatings stretch the capabilities of EIS instrumentation. Older EIS systems have the following limitations when used in this application:

- Their upper impedance limit (about $10^{10} \Omega$) is too low for good coatings.
- They are unable to make measurements on earth grounded structures.
- Their weight and size preclude field measurements.
- They are very expensive (>20 k\$).

This paper discusses the design of an EIS system not subject to these limitations. The system achieves these commissioned objectives:

- An upper impedance limit of $>10^{12} \Omega$.
- Floating operation for measurements on earth grounded structures.
- Easy portability in a personal computer.
- A DC to 100 kHz system at a low cost (<9 k\$).

The performance of the system is described in detail. This discussion includes:

- A new EIS technology - harmonic subsampling at high frequencies.
- How coating thickness affects capacitance and measurement accuracy.
- The effect of shielding, grounding and sample size on system performance.
- Special considerations for field measurements.
- Software for data acquisition and modeling.

Experimental and Instrumental Considerations in Measurements of Extremely Good (High Impedance) Coatings

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High Impedance coatings provide special challenges to the experimentalist and to the instrument designer. Many of the instrumental designs and experimental details which are unimportant for only moderate Impedance coatings are unsatisfactory for extremely good coatings. The effects of electrometer's input Impedance, stray capacitance, and input and offset currents will be discussed. The role of the sensitivity of the analyzer will also be discussed.

Non-Electrochemical Assessment Techniques

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A review of the non-electrochemical techniques used for evaluating the integrity of organic coatings and paints on steels reveals methodologies which depend on radiative or spectroscopic processes, mechanical properties of the coating, calorimetry, use non-faradaic electrical methods or protocols involving combinations of all of these categories. Several laboratories have used many of these methods over the years. Spectroscopic methods involving the interaction of the coating with radiation are too numerous to detail in great depth. Useful methods involving mechanical properties of the coating and the coating to metal bond include several acoustic imaging methods as well as acoustic emission which is particularly sensitive to bond breaking. Non-electrochemical electrical methods entails dielectrometry, but also includes recently resurged Kelvin probe methods which sense the work function of the coating substrate as modified by local dipole layers and volta potentials.

A number of issues involved in non-electrochemical methods are those of sensitivity/selectivity, relevance to corrosion, ease of application and interpretation.

Some specific examples from several of these categories are described. They include thermography, surface analysis of disbond zones as prepared using in situ cells for direct transfer to the ultra-high vacuum (UHV), acoustic emission, acoustic imaging, and Kelvin probe methods.

Thermographic imaging holds great promise particularly in light of recent advances in image processing and portability of the methods. Thermographic imaging readily detects coating defects and heterogeneities which modify emissivity, reflectivity and transmissivity, and under-film corrosion products that modulate emissivity and reflectivity.

A cell which allows electrochemical disbonding and direct transfer of the disbond surface to UHV for surface analysis has lead to important findings relative to cathodic disbonding mechanisms. The local pH has been determined to be above 13 and the role of iR drop within the disbond zone has been characterized. Compared to a bare surface, less oxide reduction for a given level of polarization can occur in the disbond zone under a coating as a result of iR drop.

Work by Haruyama and coworkers demonstrated that acoustic emission coming from a cathodically polarized substrate can provide information on coating performance and water uptake. The work relied on distinguishing the different types of emissions on the basis of frequency, amplitude and duration.

A number of acoustic imaging methods have been considered. Scanning acoustic microscopy (SAM) has been used extensively in Cambridge (UK) and at Rockwell (US) for direct in situ, real-time observation of cathodic disbonding about a polarized scribe. Similar acoustic images have been observed by the two groups, but with some differences in interpretation.

Not involving current passage, Kelvin probe methods are not dominated by defects and, hence, have recently been demonstrated to sense the potential under disbonding regions of the paint film.

In summary, electrochemical methods best characterize coating defects and water transport, but corrosion induced disbonding requires other methods or other methods in concert with electrochemical methods.

Improved Quantitative Failure Analysis for the Prediction of Coating Service Life

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Ocean City Research Corp.**

Currently, the majority of coating evaluations and ratings done in the field and laboratory involve the use of subjective visual standards. Generally, these ratings are vary dependant on the judgement of the inspector and on the environment in which the inspection is done (e.g., lighting, accessibility, vantage point). Because of these factors the rating scales are not amenable to the detailed analysis necessary for life prediction.

The development of an improved rating technique is necessary to allow the use of advanced statistical and probabilistic techniques necessary for meaningful life prediction. There are a wide variety of tools available from other industries that allow meaningful evaluation for predictive purposes. However, the protective coating industry lacks an appropriate metric upon which to utilize these techniques. Development of improved visual rating techniques will provide the objective, quantitative data necessary to develop empirical models that will allow life prediction.

This presentation centers on test results for thirteen coating systems applied over four different steel surfaces. For each coating/surface preparation, duplicate panels were exposed in each of three environments. This presentation concentrated on those panels exposed at the Ocean City Research marine test site. The improved inspection methodology was used to quantify the percent area corroded in three areas on each test panel. Thus six data values were obtained for each system, allowing statistical analysis of the results. The results presented in this presentation were limited to the average predicted life based on the test panel condition determined at five intervals spaced over three years. The test panel condition after five years was compared to the prediction based on three year data.

The predictions from the three year results showed that:

- ▶ Life predictions based on fitted three year data are somewhat optimistic given the panel condition after five years. This suggests an increasing rate of failure after initiation.
- ▶ The results demonstrate the need for probabilistic data analysis. Some coating systems demonstrated a range of behavior even over just two test panels.
- ▶ The better performing coating systems had minimal or no visible rusting after three years. No visual technique is useful for predicting service life if no failure is observed. Thus, the industry still needs to pursue analytical techniques capable of predicting the initiation of failure.

Quantitative Analysis of Surface Defects in Natural Degradation using Image Processing

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Abstract

Analysis of surface defects due to weathering degradation has been mostly dependant upon pseudo-qualitative / pseudo-quantitative comparative methods. Pictorial Standards of Coatings Defects published by the Federation of Societies for Coatings Technology is an example of a such method. The comparative method has been used to give rough ratings when the degree of degradation judged by a human inspector is compared against a pictorial guide. However, this technique cannot provide quantitative answers with scientific precision since the results are based on qualitative judgements of human perception. Analysis of surface defects is an after-failure-analysis for a coating system. A failure analysis is an important part of an experiment since an understanding of a failure mode provides tools in determining cause, preventing future failure, and aiding in placing liability. A failure analysis that leads to an understanding of a failure mechanism is a vital portion of an experiment. In this respect, the human inspection can offer little information about physical aspects of a failure mechanism.

Digital image processing / analysis has been proven to be an accurate scientific data acquisition system implemented in various of fields of science. Implementing a digital imaging technique in analysis of surface defects can provide scientific quantitative answers. With the rapid advancement of micro computing technology, digital imaging techniques have become an appealing technology for affordable implementation. Digital imaging processing / analysis technology cannot only overcome shortcomings of a human visual evaluation but also be provided as an analytical tool to help understand physical aspects of failure mechanisms.

**An Iron K-edge XANES Study of Iron and Iron Oxides for the Cathodic
Disbonding of Fusion Bonded Epoxy in Alkaline Aqueous Solution**

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ABSTRACT

Iron K-edge x-ray absorption near-edge structure (XANES) of model oxide systems was studied to help understand the mechanism of cathodic disbonding of fusion bonded epoxy (FBE) from underground steel pipelines. Two model systems were studied: (1) thin film iron (500 Å thick) thermally oxidized at 240°C; and (2) thin film iron coated with FBE and cathodically disbanded. The thin film iron exhibited a trend of decreasing metallic character with increasing thermal oxidation times. After 122 hours of oxidation, the oxidic character became predominant. The oxide appeared to be a mixture of Fe_2O_3 and Fe_3O_4 . The XANES data for the region under the cathodically disbanded FBE coating showed more metallic character than the region that maintained the bond integrity. Under the cathodic disbonding conditions of the present study (-1.5 V-SCE in 1M KOH aqueous solution), the XANES results, although preliminary, support the oxide reduction and/or oxide dissolution mechanisms of disbonding.

SENSING WATER SORPTION AND DIFFUSION IN MULTI-LAYER PROTECTIVE COATINGS VIA FLUORESCENCE PROBE TECHNIQUES

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A particular class of fluorescence probes known as molecular "rotors" has been employed in studies in single- and multi-layer protective coatings for sensing water sorption and diffusion. The fluorescence of these probes exhibit sensitivity to local mobility of the polymer matrix. In particular, when these molecules absorb light of a particular wavelength, they return to their ground electronic states by one of two pathways. If rotations around particular bonds are allowed during the nanosecond lifetime of the excited state, the molecules dissipate the energy by bond rotation. However, if the bond rotation cannot occur on the nanosecond lifetime of the excited state, then the molecules return to the ground state by emission of photons or fluorescence. The presence of water in the coatings results in "plasticization" or increased local mobility of the polymer coatings and hence an increase in bond rotation and a reduction in fluorescence intensity. For the rotor probes and protective coatings studied to date, there is a one-to-one proportionality between the amount of water sorbed in a particular (single-layer) coating and the reduction of fluorescence, with 50% reductions in fluorescence observed in coatings that sorb 4 to 5 wt% water at equilibrium. Thus, fluorescence allows for highly accurate characterization of average water concentration within a coating. Beyond allowing for characterization of sorbent content, this fluorescence technique can allow for determination of the diffusion coefficient, D , of water in a polymer film ($D=3.0 \times 10^{-8} \text{ cm}^2/\text{s}$ is measured for water in polyvinylacetate and an order of magnitude smaller in an epoxy protective coating). A high degree of accuracy and reproducibility is observed in repeated in situ sorption and desorption measurements. Most importantly for protective coatings, this technique allows monitoring of water uptake in individual layers of multi-layer coatings which is otherwise very difficult to measure. Examples of water uptake in multi-layer coatings which provide very good quantitative agreement to theoretical predictions will be provided.

METHODOLOGY FOR ASSESSING PERFORMANCE OF CORROSION INHIBITIVE ORGANIC COATINGS

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ABSTRACT

Corrosion inhibitor mechanisms in model epoxy coating systems on aluminum were studied with electrochemical impedance spectroscopy (EIS), where the emphasis of the work was on the eventual formulation of non-toxic corrosion inhibitors into barrier-type zero discharge organic coatings (ZDOC) such as powder, UV-curable, and electrocoat systems. A methodology was developed based on EIS measurements on coating-metal systems comprised of barrier coatings with defects, porous coatings, and variable inhibitor location (in coating or electrolyte) whereby the effectiveness of an inhibitor could be assessed in one week. Inhibitor effectiveness was found to be critically dependent on the ability of the electrolyte to transport the inhibitor to the coating-metal interface. Incorporation of inhibitor into a porous epoxy coating rendered the inhibitor ineffective.

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"Are We Ready for Prime-Time -
A Skeptical View on Quantitative Techniques for Coating Evaluation"

Simon K. Boocock
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The speaker will provide a critical view of the perceived or actual capabilities of a variety of approaches to improved coating evaluation, including quantitative methods. The presentation builds on the foundation of technology evaluation projects conducted for the then Navy Civil Engineering Laboratory and for the National Shipbuilding Research Program in early 1991 and late 1988.

Specific techniques highlighted in this review will include: quantitative visual analysis, electrochemical techniques, reliability analysis (and experimental design), and short-term accelerated test methods.

Some Practical Thoughts on Using and Analyzing Electrochemical Impedance Spectroscopy Data

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Abstract

A significant number of papers on electrochemical impedance spectroscopy (EIS) have focused on models for EIS spectra, and using the Kramers Kronig equation to evaluate data consistency. This paper complements these works by discussing: 1) how to cope with EIS data variability, 2) statistical validation of equivalent electrical circuit models (EECMs), and 3) guidelines for determining what physical processes are being characterized by parameters extracted from EIS spectra.

Variability is a way of life.[1-6] One way to account for variability is to use the appropriate number of repetitions for each experimental variable under study. One must balance the answer between two experimental design questions when choosing the number of repetitions: 1) What is a practical number of repetitions? and 2) How wrong do you want to be? Our experience has been that from five to ten repetitions is a reasonable compromise between these two questions.[6]

Regression analysis (curve fitting, or modeling) on equivalent electrical circuit models (EECMs) is used to derive metallic corrosion and coating parameters from EIS spectra. There must be enough degrees of freedom in a data set (each data point is a degree of freedom) when performing regression analysis; that is, the number of data points (degrees of freedom) should exceed the number degrees of freedom consumed by the regression process.[7] The process of regressing (modeling) an EECM around the data and the adjustable parameters in an EECM each consume one degree of freedom. Consequently, there should be at least two more data points than the number of adjustable parameters in an EECM. The R-squared statistic (often called the correlation coefficient) is most commonly used to validate a given EECM. It is important to remember that this statistic only measures how much of the data's variability is accounted for by the EECM.[8] Consequently, other statistics should be used in conjunction with R-squared. There are several assumptions underlying regression analysis: 1) differences between predicted (EECM) and experimental values are randomly distributed, and 2) these differences sum to zero.[9] Plotting residuals (differences) as a function of frequency is a simple, yet powerful, method for validating an EECM. Residuals should be randomly distributed around zero difference, and their sum equal to zero for a statistically valid EECM fit to a data set.[10] Chi-square is also another statistic used to validate EECM fit to an EIS spectra, and an ideal EECM has a associated Chi-square equal to zero.[11]

Capacitance magnitude can be used to determine what type of physical process is associated with a given resistance. Capacitances on the order of microFarads are typically associated with metallic corrosion;[12] nanoFarad capacitances are associated with coating (pore) resistance;[13] milliFarad capacitances are due to metallic oxides;[14]

capacitances due to absorption are on the order of 10^{-4} Farads;[15] and capacitances less than nanoFarads should be suspected as being due to parasitic pathways.[16]

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FEASIBILITY OF USING ARTIFICIAL NEURAL NETWORKS

WITH E. I. S. DATA ON COATED STEEL

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ABSTRACT

Electrochemical impedance spectroscopy (E. I. S.) techniques can provide information about the condition of protective coatings on steel marine structures. Currently, an expert is required to interpret the data produced from an E. I. S. measurement, classifying the coating as good or poor, or identifying the data as bad. This limits the use of E. I. S. techniques to experienced operators. If the E. I. S. technique is to be used for production, by in-experienced operators, measurements must be classified automatically. This investigation uses artificial neural networks (ANN) to develop an automated E. I. S. data classifier. ANN's were trained with a large data base of measurements on known good or poor coatings, and with some bad data, and were tested with E. I. S. data not included in the training set. A variety of measurement signal processing schemes and network structures were evaluated. ANN's were developed which can accurately determine if the coating is good or poor, and whether measurement problems produced bad data.

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13. ABSTRACT (Maximum 200 words) The Annapolis Detachment of the Naval Surface Warfare Center, Carderock Division (NSWCCD) was host to the "2nd Workshop on Quantitative Methods for Evaluation of Paint Coating Performance" on 1-3 November 1995. The workshop, co-sponsored by Mr. Ivan L. Caplan (NSWCCD) in conjunction with Dr. A. John Sedriks of the Office of Naval Research, was organized and chaired by Dr. John Murray of the Corrosion Branch (Code 613). Dr. Harvey Hack (Code 613) led the closing discussion session on 3 November. This report constitutes the Workshop Summary Report. Following the initiating general overview of the status of the Navy Paint systems, 23 presentations were made by internationally and nationally recognized experts covering the major types of non-destructive tests for coating systems, both electrochemical and visual assessment techniques. In addition to NSWCCD Annapolis, Philadelphia and White Oak personnel, approximately 40 people listened to the leading university, industrial research and instrument manufacturer personnel present and discuss the recent results using new research approaches, electrochemical impedance spectroscopy (EIS), electrochemical noise, dc and dc pulse approaches, as well as the improvements in enhanced visual imaging techniques.				
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